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To Mr. F.J. Kee
Director of Research

LASER ENRICHMENT OF CARBON-14

L. Mannik

A paper summarizing results obtained in research on the ultraviolet laser dissociation of formaldehyde as a method of enriching carbon-14 has been accepted for publication in Applied Physics. The dependence of the $^{14}C:^{12}C$ enrichment factor on laser linewidth, formaldehyde temperature and pressure, and degree of ^{14}C depletion has been measured and analyzed. Applications to groundwater dating and to the enrichment of ^{14}C from CANDU operating wastes are assessed.

PREFACE

One of the many beneficiaries of the Research Division's earlier laser heavy water research program has been an investigation of the enrichment of carbon-14 using the selective ultraviolet laser dissociation of formaldehyde. This technique, which yielded high enrichment factors in deuterium separation, has produced similar results with carbon-14 and this is of interest to two nuclear-related applications. Pre-enrichment of carbon-14 can lead to improvements in radiocarbon dating, especially for groundwater dating as applied to the selection of potential nuclear waste disposal sites. The laser enrichment of carbon-14 also represents an alternative to cryogenic distillation as a method of enriching carbon-14 from CANDU operating wastes to a level suitable for commercial sale. A paper summarizing our research in this area has been accepted for publication in Applied Physics. The text of the paper is given in the Appendix A.

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APPENDIX A

LASER ENRICHMENT OF CARBON-14

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ABSTRACT

An experimental study has been performed of the carbon-14 enrichment achievable in the ultraviolet laser dissociation of mixtures of $^{14}CH_2O$ and $^{12}CH_2O$. The $^{14}C:^{12}C$ enrichment factor in the CO product has been measured at 352.2 nm as a function of laser linewidth, formaldehyde temperature and pressure, and degree of carbon-14 depletion. The enrichment decreases with an increase in each of these parameters; the highest enrichment, 1190, was measured at 0.02 cm^{-1}, 303 K, 1 Torr and a ^{14}C depletion of 10%. The results are assessed in terms of their application to radiocarbon dating, in particular for groundwater dating required for nuclear waste disposal, and to the enrichment of ^{14}C operating wastes extracted from nuclear reactors to a level suitable for commercial sale.

The separation of isotopes using lasers has been the focus of many research projects in the past decade [1]. Among the applications of interest to the nuclear industry has been the enrichment of deuterium for the production of heavy water, which is used as a coolant and moderator in the CANDU (Canadian Deuterium Uranium) nuclear reactor [2]. A few years ago we performed a detailed study of the deuterium enrichment attainable by the selective ultraviolet laser dissociation of formaldehyde gas and its dependence on laser linewidth and formaldehyde temperature and pressure [3].

Formaldehyde (CH_2O) has a large number of discrete absorption bands in the range 300 to 355 nm and by an appropriate choice of wavelength it is possible to enrich the isotopes of carbon, hydrogen or oxygen using selective ultraviolet photodissociation. This was first demonstrated by Marling [4], who established that the products of the dissociation were either stable molecules (H_2 and CO) or radicals (H and HCO), or a mixture of the two, depending on the wavelength used in the irradiation.

Enriched carbon-14 has two potential applications in the nuclear industry. Carbon-14 generated by neutron activation in nuclear reactors represents a troublesome operating waste which is extracted using chemical methods such as ion exchange resins. Enrichment of this carbon to >90% ^{14}C would create a potentially marketable product while at the same time reducing the scale of the operating waste disposal problem. Secondly, radiocarbon dating of groundwater is a valuable tool in establishing groundwater flow patterns for the assessment of potential nuclear waste disposal sites. Pre-enrichment of the carbon-14 in a sample would have several advantages, including the possibility of dating much older samples than is currently feasible.

The latter application was the stimulus for an earlier study by Hedges et al [5] of the enrichment of carbon-14 using the ultraviolet laser dissociation of formaldehyde. Irradiation at 326.94 nm produced carbon enriched by factors up to 150 in carbon-14. The highest enrichments were obtained when NO was introduced to scavenge the radical products. It was recognized that the enrichment procedure would be simpler if longer wavelengths were used so that stable molecular products would predominate. Marling [4] has demonstrated that above 330 nm this is the case. Hedges et al also realized that the linewidth (0.14 to 0.18 cm^{-1}) and spectral purity of their ultraviolet laser were limiting the enrichment.

We have performed an investigation of the ultraviolet spectroscopy of $^{14}CH_2O$ and $^{12}CH_2O$ in the range 343 to 353 nm and have found a high selectivity wavelength (352.2 nm) at which enrichment measurements have been carried out as a function of laser linewidth and formaldehyde temperature and pressure. These were identified in the earlier deuterium enrichment studies as the key parameters affecting the enrichment factor [3]. In addition the present investigation included a study of the enrichment as a function of carbon-14 depletion since, in applying enrichment results to an actual isotope separation process, it is important to maximize the rate of generation of product, in this case ^{14}CO, which means that ^{14}C depletions greater than 50% are of primary interest.

The results of this ^{14}C enrichment study are reported along with a discussion of their implications for the two applications noted above. Before proceeding to these results a review of certain key definitions is in order. The selectivity is the ratio of $^{14}CH_2O$ to $^{12}CH_2O$ absorption coefficients as measured at a particular wavelength and laser linewidth. It will also depend on the formaldehyde temperature and pressure. The $^{14}C:^{12}C$

enrichment factor is determined from

$$EF = \frac{[^{14}CO]/[^{12}CO]}{[^{14}CH_2O]_i/[^{12}CH_2O]_i} \quad (1)$$

where the square brackets denote the number of molecules per unit volume and the subscript i refers to the initial formaldehyde sample. The ^{14}C and ^{12}C depletions are the fraction of $^{14}CH_2O$ and $^{12}CH_2O$, respectively, dissociated by the laser in the enrichment process. Assuming only molecular products, which is a valid assumption at 352.2 nm [4], each formaldehyde dissociation yields one carbon monoxide molecule. Therefore, in terms of the quantities in (1), the two depletions can be written as

$$D^{14} = [^{14}CO]/[^{14}CH_2O]_i \quad (2)$$

and

$$D^{12} = [^{12}CO]/[^{12}CH_2O]_i \quad (3)$$

These three equations can be combined to yield

$$EF = D^{14}/D^{12} \quad (4)$$

1. EXPERIMENTAL PROCEDURE

1.1 Spectroscopy

In order to identify regions of high selectivity, spectra of ^{14}C-formaldehyde and natural abundance formaldehyde were recorded in a dual cell absorption experiment similar to that used in earlier deuterated formaldehyde studies [3]. Simultaneous spectra were recorded using a Nd:YAG pumped dye laser and absorption cells consisting of a 1.3 m long cell for the $^{14}CH_2O$ which was set up for two passes and a 2.3 m long multipass cell for the $^{12}CH_2O$ which was aligned for 80 to 100 passes. The survey scan, which ranged from 343 to 353 nm, was performed with a laser linewidth of 0.11 cm^{-1}. Subsequently higher resolution spectra were recorded at high selectivity wavelengths using an external Fabry-Perot interferometer to narrow the linewidth to 0.02 cm^{-1}.

^{14}C-formaldehyde was purchased from Amersham in the form of para-formaldehyde powder with an activity of 579 μCi/mg, corresponding to a ^{14}C concentration of 29%. In order to prevent polymerization, the absorption cells were heated to 343 K.

1.2 Enrichment Measurements

While the apparatus for carbon-14 enrichment measurements is essentially the same as that used in earlier deuterium enrichment studies [3] there were several revisions to the experimental procedure which are outlined below.

Briefly, a mixture of ^{14}C-formaldehyde and natural abundance formaldehyde (99% $^{12}CH_2O$, 1% $^{13}CH_2O$) was irradiated with the laser tuned to the desired wavelength (352.2 nm for the measurements reported here) by monitoring the absorption of $^{14}CH_2O$ in a reference cell. The laser output energy in the ultraviolet was typically 3 to 4 mJ at a linewidth (FWHM) of 0.11 cm^{-1}. Narrow linewidth (0.02 cm^{-1}) was achieved by using an external Fabry-Perot interferometer which reduced the output energy by a factor of 30 to 50. After the undissociated formaldehyde was frozen out with liquid nitrogen, the carbon monoxide and hydrogen dissociation products were analyzed with a mass spectrometer.

After initial tests of this procedure, it was noted that the ^{14}C-formaldehyde was gradually dissociating as a result of contact with the hot metal walls of the reference cell. Rather than constructing a glass cell to overcome this problem, it was decided to use CHDO as the reference material, since a fresh supply could be introduced for each experiment unlike the expensive and radioactive $^{14}CH_2O$. This technique is feasible because in the spectra of the isotopic formaldehydes near 352.2 nm (Fig. 1) there is a shoulder and an absorption minimum in the CHDO spectrum on either side of the $^{14}CH_2O$ absorption maximum which can be used as reference points to fix the laser wavelength.

Another factor noted in preliminary experiments was the difficulty of obtaining reproducible $^{14}CH_2O$:$^{12}CH_2O$ mixtures in the starting samples which were prepared prior to laser irradiation. Therefore it was necessary to measure this ratio in each experiment, which made the procedure more cumbersome but yielded more consistent results. The ^{14}C sample as obtained from the supplier contained a mixture of $^{12}CH_2O$ and $^{14}CH_2O$ in a ratio of approximately 2:1. Since the ^{14}C concentration of the sample could be deduced from activity data supplied by the manufacturer, the $^{12}CH_2O$:$^{14}CH_2O$ ratio could be calculated; an uncertainty of 8% was introduced because the sample contained up to 10% water impurity. A portion of this sample was isolated prior to its combination with 1 to 10 Torr of $^{12}CH_2O$ to form the irradiation sample. After the laser irradiation and mass spectrometer analysis of products were completed, the mass spectrometer and associated plumbing were pumped on for one hour before the previously isolated sample was analyzed for its mass 30 ($^{12}CH_2O$) content,

which permitted the amount of $^{14}CH_2O$ to be deduced. In practice the irradiation sample had $^{14}CH_2O$ concentrations ranging from 3.5×10^{-5} to 8×10^{-4} (mole fraction).

The mass spectrometer analysis of products was also more complicated than in the deuterium enrichment measurements. For narrow linewidth measurements at reduced laser energy the amount of ^{12}CO produced could not be accurately determined from the mass 28 signal because of interference from nitrogen present as a result of small air leaks and outgassings in the vacuum system. Therefore it was deduced from the measured H_2, ^{13}CO and ^{14}CO signals, using the fact that formaldehyde dissociation at 352 nm produces equal amounts of H_2 and CO [4], so that

$$[^{12}CO] = [H_2] - [^{13}CO] - [^{14}CO] \ . \qquad (5)$$

This equality was verified experimentally by irradiating a sample of $^{14}CH_2O$ at 352.2 nm and noting that equal amounts of H_2 and ^{14}CO were generated. For broad linewidth, higher energy irradiations the amount of ^{12}CO produced was large enough to be accurately measurable above the background N_2 signal. On the other hand, the relatively large amount of ^{12}CO introduced a new correction due to the presence of $^{12}C^{18}O$ which interferes with the $^{14}C^{16}O$ signal at mass 30. This made it necessary to perform background laser irradiations on $^{12}CH_2O$ with no $^{14}CH_2O$ present so that any mass 30 generated would be due to $^{12}C^{18}O$. In this way it was established that the $^{12}C^{18}O$ correction amounted to 0.5% of the $^{12}C^{16}O$ signal. (Note that since the natural abundance of ^{18}O is only 0.2% of ^{16}O, laser irradiation at 352.2 nm yields a 2.5-fold enrichment in ^{18}O.) Thus in a normal irradiation, the amount of $^{14}C^{16}O$ product was the observed mass 30 signal minus 0.5% of the $^{12}C^{16}O$ product. The magnitude of the $^{12}C^{18}O$ correction ranged from 10 to 50% of the total mass 30 signal.

The measured values of both enrichment and depletion are estimated to be accurate to within ±20%.

2. ENRICHMENT MEASUREMENTS: RESULTS AND DISCUSSION

2.1 Dependence on Laser Linewidth, Pressure, Temperature

The survey of the ultraviolet spectra of $^{12}CH_2O$ and $^{14}CH_2O$ identified one absorption band in the latter with the potential for high $^{14}C:^{12}C$ enrichment factors. This band, centered at 352.2 nm, is shown in Figure 1 along with the spectra of $^{12}CH_2O$ and $^{12}CHDO$ in the same region. All the enrichment measurements were performed with the laser tuned to this wavelength.

The $^{14}C:^{12}C$ enrichment factor was measured at two laser linewidths for a constant ^{14}C depletion (20%), pressure (1 Torr) and temperature (343 K). The result is that the enrichment increased by a factor of 2.5 (220 to 546) when the linewidth was reduced from 0.11 cm^{-1} to 0.02 cm^{-1}. Similar results were obtained in the deuterium enrichment studies using formaldehyde [3]. This dependence is a result of a broad laser linewidth accessing regions of lower ^{14}C and higher ^{12}C absorption, thereby giving a lower enrichment (cf Fig. 1). The narrower laser linewidth confines the irradiation to the peak of the 0.1 cm^{-1} wide $^{14}CH_2O$ absorption band.

At constant ^{14}C depletion (20%), laser linewidth (0.02 cm^{-1}) and formaldehyde temperature (343 K), the $^{14}C:^{12}C$ enrichment factor decreased by nearly a factor of two (546 to 322) when the formaldehyde pressure increased from 1 to 10 Torr. A similar pressure dependence was observed in the deuterium enrichment studies and was explained by pressure broadening effects which reduce the strength of the $^{14}CH_2O$ absorption maximum and increase the strength of the underlying $^{12}CH_2O$ absorption, thereby lowering the enrichment factor [3].

In working with formaldehyde at pressures higher than a few Torr, it is necessary to elevate the temperature to prevent polymerization of the gas on the walls of the cell [6]. Experience from the deuterium enrichment studies indicates that at 343 K formaldehyde pressures up to 20 Torr can be handled without significant polymerization. However, because of the presence of hot bands in the $^{12}CH_2O$ absorption spectrum, such a temperature increase can be expected to reduce the enrichment factor [3]. This was confirmed in the present study, since for a constant ^{14}C depletion (10%), linewidth (0.02 cm^{-1}) and pressure (1 Torr), the $^{14}C:^{12}C$ enrichment factor decreased from 1190 to 655 when the temperature was raised from 303 to 343 K.

To our knowledge, the enrichment of 1190 measured at 1 Torr, 0.02 cm^{-1} and 303 K represents not only the highest single step enrichment factor observed for isotopes of carbon but also the highest enrichment factor measured for any isotope in a single photon dissociation experiment.

2.2 Dependence on Carbon-14 Depletion

Figure 2 summarizes the results of a study of the dependence of the $^{14}C:^{12}C$ enrichment factor on the carbon-14 depletion (D^{14}) for three pressures at constant temperature (343 K) and laser linewidth (0.11 cm^{-1}). The observed decrease of enrichment with increasing depletion of the rare isotope is expected from theoretical considerations [7], although the exact form of the relationship will depend on the details of the irradiation

geometry. The rapid decrease observed here is indicative of the non-optimized design of the irradiation cell. For an optimized design the enrichment at 50% depletion can be as high as 75% of the enrichment at 10% depletion [7].

Since depletion was not considered in the previous investigation of deuterium enrichment, its role will be examined in greater detail. For the purposes of analysis it is useful to plot the depletion against Et, the product of the laser energy per pulse entering the irradiation cell and the duration of the irradiation. This parameter is a measure of the total number of photons incident on the gas in the irradiation cell. This is done in Fig. 3 for both D^{14} and D^{12}, with the latter being calculated from the experimental data using (4).

In this form the data can be used to describe the evolution of the enrichment process and to analyze the experimental observations from a theoretical point of view. The details of this analysis, which leads to the dashed curves shown in Fig. 3, are given in the Appendix. The analysis demonstrates that there is no fundamental difference between D^{14} and D^{12}: they each vary exponentially with Et, viz

$$D = 1 - \exp(-K\alpha\, Et) \qquad (6)$$

where α is the absorption coefficient at 352.2 nm for $^{14}CH_2O$ or $^{12}CH_2O$, depending on whether D^{14} or D^{12} is being evaluated. The only difference is that $\alpha_{12} \ll \alpha_{14}$ because a wavelength with a high selectivity has been chosen.

For the present experimental conditions $K\alpha_{12}\, Et \ll 1$ so that (6) gives $D^{12} \approx K\alpha_{12}\, Et$, resulting in the observed linear relationship. For D^{14}, because of the much larger absorption coefficient, a linear dependence only applies for small values of Et. As Et increases the number of $^{14}CH_2O$ molecules available to absorb the laser radiation is reduced by dissociation, with the result that there is a slower rate of increase of the carbon-14 depletion and a nonlinear dependence of D^{14} on Et as seen in Fig. 3. If the irradiation were allowed to proceed for such a long time that the number of $^{12}CH_2O$ molecules was also significantly depleted, the relationship between D^{12} and Et would exhibit a similar nonlinear behaviour at large values of Et.

One further result of the analysis is that the initial slope of the depletion as a function of Et depends directly on the path length to volume ratio. Specifically, the constant K in (6) is given by $K = 0.63\, \ell/V$ where ℓ is the path length (m) and V is the volume (cm^3) of the irradiation cell. This means that in order to achieve a similar enrichment and depletion with a different cell it is necessary only to scale the duration of the irradia-

tion to match the particular ℓ/V ratio of the cell. For example, the present cell (ℓ = 4.5 m; V = 50 cm^3) has ℓ/V nine times larger than that of the multipass cell used for $^{12}CH_2O$ absorption spectroscopy (ℓ = 200 m; V = 20 L). Therefore, if the latter cell were used in an application of the laser enrichment of carbon-14, which is considered in Section 3.2 below, an irradiation time nine times longer would be required to obtain the same enrichment and depletion observed with the smaller cell.

3. APPLICATIONS

3.1 Enrichment of Carbon-14 From Nuclear Reactors

Carbon-14 is formed in nuclear reactors by the action of neutrons on ^{14}N, ^{13}C and ^{17}O. CANDU reactors produce significantly more carbon-14 than light water reactors because of the greater mass of moderator (D_2O) in the core. In the original design a significant fraction of the carbon-14 was generated by the (n,p) reaction on nitrogen-14 in the annulus gas between pressure and calandria tubes. Recently built CANDU reactors no longer use nitrogen for this purpose.

This waste product of nuclear reactors has a number of uses, primarily as a tracer for carbon-12 in medical, pharmaceutical and biological research. If the carbon-14 were to be recovered and enriched to 90% concentration it would have a wholesale value of $12,000 to $15,000 per gram. Presently, carbon-14 produced in CANDU reactor moderator water is extracted by ion exchange resins. The enrichment of this carbon-14 to the 90% level would create a valuable product while at the same time reducing the costs of disposa of reactor operating wastes.

A single stage enrichment process based on the selective ultraviolet laser dissociation of formaldehyde would require an enrichment factor of 170 for 5% initial carbon-14 or 890 for 1% initial carbon-14. The data reported here indicate that such enrichments are well within reach. However, a detailed engineering analysis would need to be performed to determine the optimum operating parameters (eg, pressure, temperature, laser linewidth, depletion) for a carbon-14 enrichment process. In addition, since carbon-14 is recovered as carbon dioxide or as a carbonate that can be readily converted to carbon dioxide, it is necessary to examine methods of efficiently converting CO_2 to CH_2O. One possible route would be to synthesize formaldehyde from CO_2 and H_2 using a methanation reaction as an intermediate step. The feasibility of such as process has been demonstrated and an operating laboratory-scale system was built and tested [8]. Complete conversion of CO_2 to CH_2O was achieved with a production rate of 1.5 g/h of formaldehyde.

3.2 Radiocarbon Dating

Carbon dating as a method of determining the age of an unknown sample has been in existence for more than thirty years. Conventional methods infer the carbon-14 content of the sample and hence its age from a measurement of the decay rate. In the past few years direct counting techniques have emerged which are able to determine the number of carbon-14 atoms remaining in a sample by means of an ultrasensitive mass spectrometer based on the use of a tandem accelerator or cyclotron to eliminate interfering atoms or molecules with the same mass. Accelerator-based mass spectrometry is capable of dating samples containing milligrams of carbon as compared to the grams required by conventional carbon dating [9].

These new methods are still limited to the same maximum age as conventional carbon dating, approximately 50 000 years. In addition, the time required for an age measurement can be considerable; for example, assuming an accelerator with an ion source current of 50 μA and a 1% collection efficiency a 50 000 year old sample would require 3 h of counting to achieve an accuracy of 10%. Therefore, various groups have considered combining accelerator techniques with pre-enrichment of the carbon-14 concentration. Isotopic enrichment increases the counting rate by a factor equal to the enrichment, thereby reducing the time required for sample analysis and making feasible the carbon dating of older samples.

Several different enrichment techniques have been considered for carbon dating. Thermal diffusion was used to obtain a six-fold enrichment which extended the range of carbon-14 dating to 75 000 years [10], but the enrichment process required several weeks. Electromagnetic isotope separation has been used to enrich the carbon concentration of a sample by a factor of 500 [11], but this method is extremely wasteful of carbon sample due to incomplete ionization and losses at the ion collector. The use of lasers for the enrichment step, first suggested in 1973 [12], promises to overcome the drawbacks associated with the other methods since, as discussed below, a commercially available ultraviolet laser irradiating formaldehyde for less than two hours can dissociate 85% of the carbon-14 molecules to give an enrichment factor of 30.

This application will also require an efficient conversion of CO_2 to CH_2O. For the small samples normally encountered in carbon dating applications the CH_2O synthesis involving a methane intermediate which was described above may not be suitable. An alternative method is to first convert CO_2 to CO by passing it over hot zinc and then convert CO to CH_2O by reacting it with H_2 in the presence of mercury. The latter technique has been used

to prepare isotopic formaldehyde [4] and the former has been demonstrated in the laboratory with a conversion efficiency approaching 100% [13].

One aspect of the application of pre-enrichment to carbon dating which has not been made clear in previous discussions is its effect on the sample size. The accelerator-based counting techniques require a minimum amount of carbon in the sample, ranging from <1 mg to several milligrams depending on the efficiency of the sample preparation procedure. The enrichment step increases the carbon-14 concentration by discarding carbon-12, thereby increasing the required starting sample size by a factor roughly equivalent to the enrichment factor. In order to clarify this point consider the following equation derived from (3) and (4)

$$EF = D^{14} \cdot [^{12}CH_2O]_i/[^{12}CO] \qquad (7)$$

The ratio $[^{12}CH_2O]_i/[^{12}CO]$ is equal to the ratio of the weight of carbon in the starting sample to that in the sample to be counted. If the minimum amount of carbon that can be readily processed by an accelerator-based mass spectrometer is 1 mg, the minimum starting sample size is EF/D^{14} mg, assuming no losses in the formaldehyde synthesis step. If a more realistic 80% conversion efficiency of CO_2 to CH_2O is assumed the result for the minimum starting sample size MSS (mg carbon) is

$$MSS = 1.25\ EF/D^{14} \qquad (8)$$

In certain applications, this means that only relatively modest enrichment factors are of practical interest because of the difficulty of obtaining larger starting samples. An example is groundwater dating for the assessment of nuclear waste disposal sites in hard rock formations which are not expected to yield very large water samples.

The $^{14}C:^{12}C$ enrichment data presented in Section 2 clearly demonstrate that there is a wide range of enrichments that can be achieved, depending on the experimental conditions. Therefore the selection of a suitable set of operating parameters becomes an important task in applying these data to the carbon dating of actual samples. From Fig. 2 the irradiation of 1 to 10 Torr of formaldehyde at 343 K with a laser linewidth of 0.11 cm^{-1} would dissociate 85% of the carbon-14 and yield an enrichment of 30. In this case the irradiation was performed for 10 minutes with a laser energy of 0.9 mJ and a repetition rate of 10 pps. From (8) this would require an initial carbon sample of 50 mg, which corresponds to 100 Torr-L of formaldehyde at 343 K, in order to

end up with 1 mg of carbon for the accelerator-based mass spectrometer. On this basis the small cell used to obtain the enrichment data would be totally unsuitable for the processing of actual samples since in the present example it would require a formaldehyde pressure of more than two atmospheres which would rapidly polymerize on the walls. However, the 20 L cell used for $^{12}CH_2O$ spectroscopy would require only 5 Torr of formaldehyde under these conditions. From the analysis of Section 2.2 the effect of the larger cell would be to increase the duration of the irradiation by a factor of nine, so that 90 minutes rather than 10 minutes of irradiation would be required with a laser energy of 0.9 mJ at 10 pps.

As noted earlier, the enrichment factor is estimated to be accurate to within 20%. This should be adequate for most carbon dating applications without the need to perform a simultaneous enrichment measurement on a reference sample, especially for older samples where the technique is most likely to be applied. For example, a 20% uncertainty in an enrichment of 30 leads to an uncertainty of <2000 years in the age determination which, for samples of 50 000 years or older, amounts to an error of a few percent.

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APPENDIX

In Figure 3 the carbon-14 and carbon-14 depletions (D^{14} and D^{12}) are plotted against the product of the laser energy per pulse entering the irradiation cell (E in mJ) and the duration of the irradiation (t in seconds) for three formaldehyde pressures. In this section expressions are derived for D^{14} and D^{12} as a function of Et.

The absorption of radiation by a gas at a pressure P (Torr) in a cell with an optical path length ℓ (m) is given by the Beer-Lambert Law

$$I = I_o \exp(-\alpha P \ell) \qquad \text{(A-1)}$$

where I_o and I are the number of photons per second exiting the cell for the cell empty and full respectively, and α is the absorption coefficient for the particular molecular species (m^{-1} $Torr^{-1}$). The implicit assumption is that α depends only on the molecular species (in this case $^{14}CH_2O$ or $^{12}CH_2O$), the temperature and the laser wavelength and is independent of pressure. This will be true at pressures low enough that pressure broadening effects are minimal. It is also assumed that the total number of absorbers does not change appreciably during irradiation, which will be the case at low depletions. Neglecting transmission losses, I_o is equal to the number of photons per second entering the cell.

With the two absorbers present simultaneously, (A-1) becomes

$$I = I_o \exp(-\alpha_{12} P_{12} \ell - \alpha_{14} P_{14} \ell) \qquad \text{(A-2)}$$

where P_{12} and P_{14} are the partial pressures of $^{12}CH_2O$ and $^{14}CH_2O$, respectively, and the absorption coefficients were measured from spectra taken at 352.2 nm (α_{12} = 9.0 x 10^{-4} m^{-1} $Torr^{-1}$; α_{14} = 0.15 m^{-1} $Torr^{-1}$). Under the experimental conditions of the enrichment measurements $\alpha_{14} P_{14} \ll \alpha_{12} P_{12}$ so that almost all the photons are absorbed by $^{12}CH_2O$ and the simpler equation

$$I = I_o \exp(-\alpha_{12} P \ell) \qquad \text{(A-3)}$$

can be used, where P is the total pressure and $P \approx P_{12}$. For the pressure range (1 - 10 Torr) and the path length (4.5 m) in the present experiments the product $\alpha_{12} P \ell \ll 1$, with the result that $\exp(-\alpha_{12} P \ell)$ can be approximated by $(1-\alpha_{12} P \ell)$.

The carbon-12 depletion D^{12}, is defined by

$$D^{12} = \frac{\text{number of } {}^{12}CO \text{ produced by laser irradiation}}{\text{number of } {}^{12}CH_2O \text{ in initial sample}} = \frac{N({}^{12}CO)}{N({}^{12}CH_2O)} \qquad \text{(A-4)}$$

Assuming unit quantum yield, ie, each photon absorbed by a $^{12}CH_2O$ molecule leads to the creation of one ^{12}CO molecule, the numerator is equal to the number of photons per second absorbed by $^{12}CH_2O$, which is given by $I_o - I$, multiplied by the irradiation time t(seconds). That is, using (A-3)

$$\begin{aligned} N({}^{12}CO) &= (I_o - I)t \\ &= I_o t[1-\exp-(\alpha_{12} P \ell)] \\ &\approx I_o t \alpha_{12} P \ell \end{aligned} \qquad \text{(A-5)}$$

The factor I_o can be calculated by using the energy per pulse ($E \times 10^{-3}$ J) and the pulse repetition rate (10 pulses per second) as well as the fact that at 352.2 nm each photon carries an energy of 5.64×10^{-19} J.

$$\text{Thus } I_o = \frac{E \times 10^{-3} \times 10}{5.64 \times 10^{-19}}$$

$$= 1.77 \times 10^{16} E \qquad \text{(A-6)}$$

Turning to the denominator of (A-4),

$$N({}^{12}CH_2O) = N_L V \frac{P}{760} \frac{273}{T} \qquad \text{(A-7)}$$

where

N_L is Loschmitt's Number = 2.69×10^{19} molecules per cm^3 at NTP.
V is the cell volume (cm^3)
T is the cell temperature (K).

Therefore $N(^{12}CH_2O) = 2.82 \times 10^{16}$ PV for T = 343 K.

The carbon-12 depletion can now be calculated:

$$D^{12} = \frac{N(^{12}CO)}{N(^{12}CH_2O)}$$

$$= \frac{1.77 \times 10^{16}\ a_{12} P \ell\ Et}{2.82 \times 10^{16}\ PV}$$

$$= 0.63\ (\frac{a_{12}\ell}{V})\ Et \qquad \text{(A-8)}$$

For the present experiments $a_{12} = 9.0 \times 10^{-4}$ m^{-1} $Torr^{-1}$, $\ell = 4.5$ m, V = 50 cm^3, so that D^{12} plotted against Et should give a straight line of slope 5.1×10^{-5}, independent of the pressure. This is shown as a dashed line in Fig. 3. Experimentally the slope is 5.7×10^{-5}. This discrepancy can partly be accounted for by the difficulty of accurately measuring a_{12}, which is a very small absorption coefficient. The addition of transmission losses and the use of a quantum yield less than 1 will tend to lower the calculated slope.

The calculation of D^{14} is complicated because the number of $^{14}CH_2O$ absorbers is not constant and also because a large fraction of the photons are absorbed by $^{12}CH_2O$. To simplify the analysis it is initially assumed that ^{12}C absorption does not play a part, ie, the calculation is done for the case of an infinitely large $^{14}C:^{12}C$ enrichment factor. Then (A-1) can be applied to the $^{14}CH_2O$ absorbers, with P_{14} being a function of time. This is handled by expressing P_{14} in terms of $N(^{14}CH_2O)$ using an equation analogous to (A-7)

$$P_{14}(t) = \frac{N(^{14}CH_2O)\ 760\ T}{N_L\ V\ 273} \qquad \text{(A-9)}$$

$$= c^{14}N(t)$$

where $N(^{14}CH_2O)$ is a function of time ($^{14}N(t)$) and c is a constant.

The number of photons absorbed per second is equal to the rate of decrease of the number of $^{14}CH_2O$ absorbers, again assuming unit quantum yield. Therefore, neglecting mirror losses in the irradiation cell

$$\frac{d^{14}N}{dt} = -(I_o - I)$$

$$= -I_o[1-\exp(-\alpha_{14}P_{14}\ell)] \qquad \text{(A-10)}$$

$$= -I_o[1-\exp(-c\alpha_{14}\ell^{14}N)] \ .$$

Rewriting and integrating this equation gives

$$\int_{^{14}N(o)}^{^{14}N(t)} \frac{d^{14}N}{1 - \exp(-c\alpha_{14}\ell^{14}N)} = \int_o^t - I_o dt \qquad \text{(A-11)}$$

For $c\alpha_{14}\ell^{14}N \ll 1$, which applies to the present experiments, the equation has the solution

$$^{14}N(t) = {}^{14}N(o)\ \exp(-I_o\ c\alpha_{14}\ell t) \qquad \text{(A-12)}$$

Therefore the carbon-14 depletion can be calculated:

$$D^{14} = \frac{^{14}N(o) - {}^{14}N(t)}{^{14}N(o)}$$

$$= 1 - \exp(-I_o\ c\alpha_{14}\ell t) \qquad \text{(A-13)}$$

Substituting (A-6) and the values of the constants this reduces to

$$D^{14} = 1 - \exp(-8.48 \times 10^{-3}\ Et) \qquad \text{(A-14)}$$

This relationship is plotted as a dashed curve in Figure 3. In the initial stages of the irradiation (low Et) the calculated curve represents the experimental data reasonably well but at higher values of Et the calculation overestimates the depletion. The addition of mirror losses and absorption by the $^{12}CH_2O$ will tend to lower the curve, making the agreement between calculation and experiment better at high values of Et and worse at low Et.

If the evolution of D^{12} at high Et were of interest, a similar derivation would give

$$D^{12} = 1 - \exp(-I_o\ c\alpha_{12}\ell t)$$

$$= 1 - \exp(-5.1 \times 10^{-5}\ Et) \qquad \text{(A-15)}$$

which for low values of the exponent reduces to the same result as that given by (A-8).

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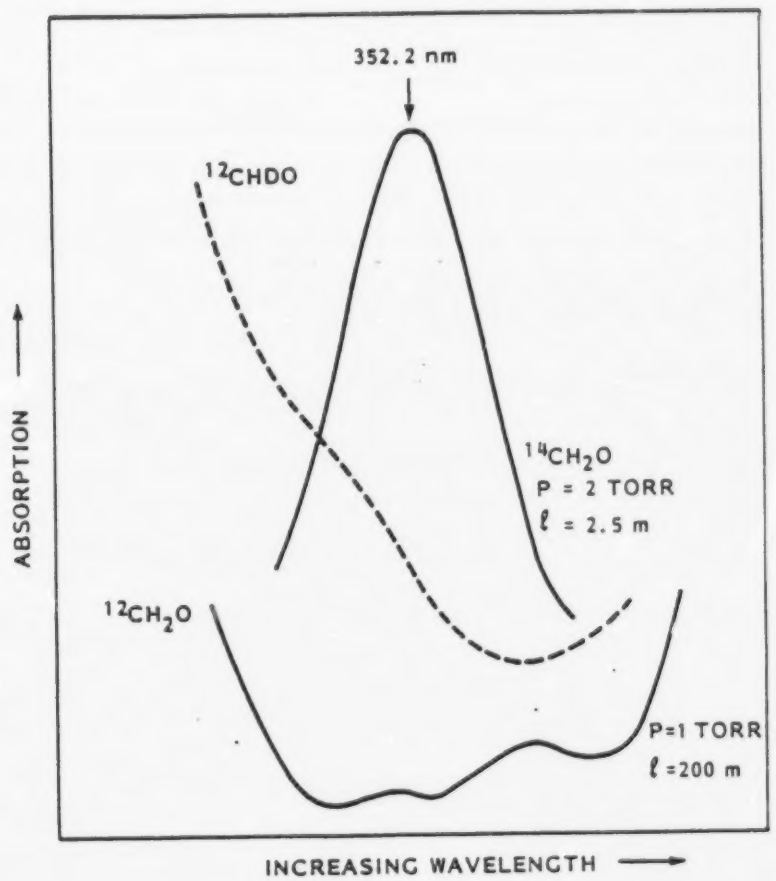

FIGURE 1

ABSORPTION SPECTRA OF $^{12}CH_2O$, $^{12}CHDO$ AND $^{14}CH_2O$ NEAR 352 nm MEASURED WITH A LASER LINEWIDTH OF 0.11 cm^{-1}. THESE REPRESENT CHART PAPER TRACES OF THE RATIO OF TRANSMITTED TO INCIDENT ENERGY. AT 352.2 nm THE ABSORPTION COEFFICIENTS ARE 0.15 m^{-1} $TORR^{-1}$ FOR $^{14}CH_2O$ AND 9.0×10^{-4} m^{-1} $TORR^{-1}$ FOR $^{12}CH_2O$. THE FWHM LINEWIDTH OF THE $^{14}CH_2O$ BAND IS APPROXIMATELY 0.1 cm^{-1}.

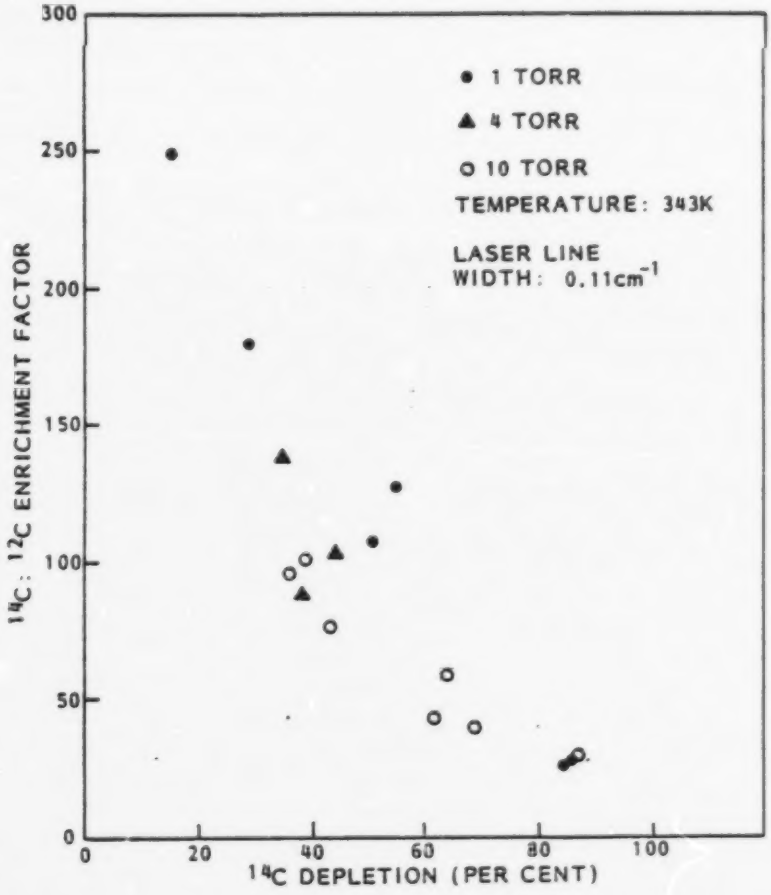

FIGURE 2

DEPENDENCE OF THE ^{14}C : ^{12}C ENRICHMENT FACTOR ON CARBON-14 DEPLETION

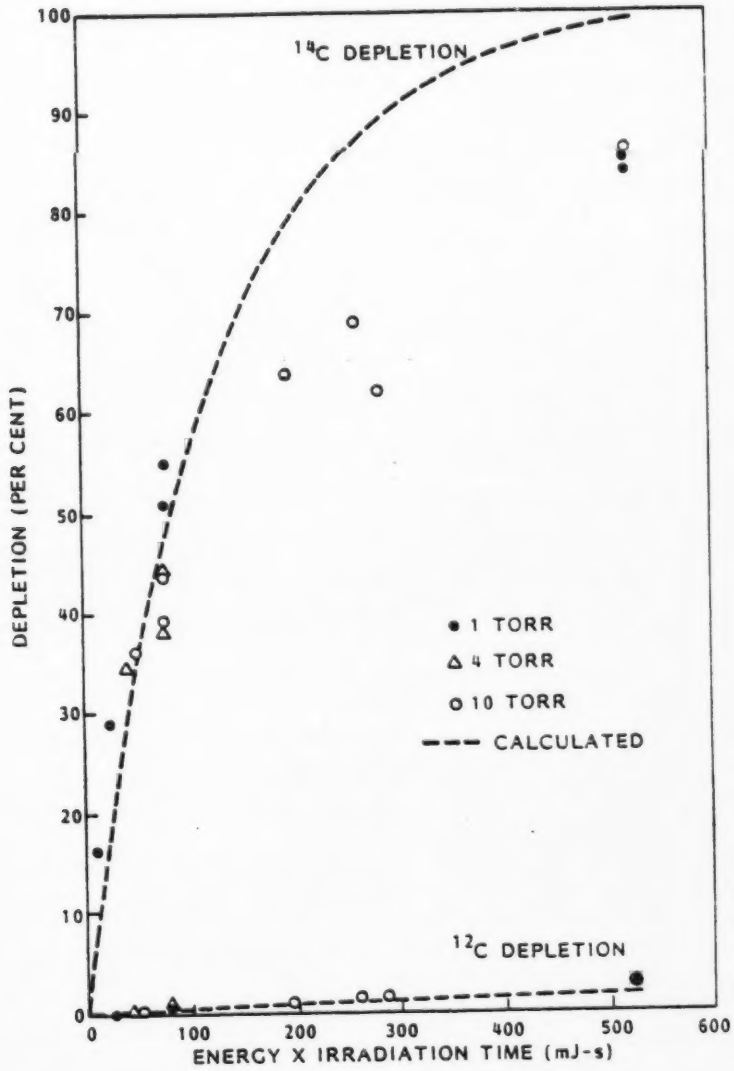

FIGURE 3

VARIATION OF CARBON-14 AND CARBON-12 DEPLETION WITH THE PRODUCT OF LASER ENERGY AND DURATION OF IRRADIATION. THE DASHED LINES RESULT FROM A CALCULATION OF THE DEPENDENCE AS DETAILED IN THE APPENDIX.